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(54) Title: FLUORINATED DIESTER

(57) Abstract

Fluorinated diesters useful for imparting repellency of low surface tension fluids to thermoplastic polymers of formulae: R_f-O-C(O)-$(CH_2)_n$-C(O)-O-R_1; R_f-O-C(O)-CH_2-CH(R_2)-C(O)-O-R_f, a mixture of R_f-O-C(O)-$(CH_2)_n$-C(O)-O-R_1, R_f-O-C(O)-$(CH_2)_n$-C(O)-R_f, and R_1-O-C(O)-$(CH_2)_n$-C(O)-O-R_1; and $[F(CF_2)_xCH_2CH_2\text{-S-}CH_2]_2\text{-C-}[CH_2\text{-O-C(O)-}C_{17}H_{35}]_2$; wherein R_f is $F(CF_2)_x$-$(CH_2)_m$ wherein x is 4 to 20 and m is 2 to 6, or $F(CF_2)_x$-$SO_2N(R_3)$-R_4 wherein x is 4 to 20; R_1 is a saturated aliphatic hydrocarbon with an average carbon chain length of 12 to 66 carbons; R_2 is a saturated or unsaturated hydrocarbon with 1-20 carbon atoms; R_3 is an alkyl radical having 1 to 4 carbon atoms; R_4 is an alkylene radical having 1 to 12 carbon atoms; n is 1 to 20, and x is 4 to 20 are disclosed.

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TITLE

FLUORINATED DIESTER

FIELD OF THE INVENTION

This invention relates to certain fluorinated diesters and to a process for imparting superior repellency of low surface tension fluids to thermoplastic polymers, in particular fibers, fabrics, nonwovens, films, and molded articles by the addition of the diesters to the polymer melt.

BACKGROUND OF THE INVENTION

Thermoplastic polymer fibers are frequently treated with fluorochemical compounds in order to affect the surface characteristics of the fiber, for example to improve water repellency or to impart stain or dry soil resistance. Most frequently, fluorochemical dispersions are applied topically to the fabrics made from these fibers by spraying, padding or foaming, followed by a drying step to remove water.

For example, a method is known for obtaining dry soil resistance and nonflame propagating characteristics in a textile fiber by applying topically aqueous dispersions of a variety of fluorinated esters derived from perfluoroalkyl aliphatic alcohols of the formula $C_nF_{2n+1}(CH_2)_mOH$ where n is from about 3 to 14 and m is 1 to 3, together with mono- or polycarboxylic acids which contain from 3 to 30 carbons and can contain other substituents. The fluorinated esters include, among

others, a perfluoroalkylethyl stearate corresponding to "ZONYL" FTS, as well as perfluoroalkylethyl diesters made from dodecanedioic acid or tridecanedioic acid.

It is well recognized that the process of manufacturing thermoplastic polymeric fibers and fabrics could be simplified and significant capital investment could be eliminated if the topical application were replaced by incorporating a fluorochemical additive into the polymer melt prior to the extrusion of the fiber. The difficulty has been in finding suitably effective fluorochemical additives.

Thermoplastic polymers include, among others, polyolefins, polyesters, polyamides and polyacrylates. Polyolefins, and in particular polypropylene, are frequently used for disposable nonwoven protective garments, particularly in the medical/surgical field, in part because of a polyolefin's inherent water-repellency. However, polyolefins are not inherently good repellents for other lower surface tension fluids frequently encountered in the medical field such as blood and isopropyl alcohol. To get around this deficiency, fluorochemical dispersions are applied topically to these fabrics.

The requirements of an additive suitable for incorporating into a polyolefin melt include, besides the ability to repel low surface tension fluids at a low concentration of the additive, a satisfactory thermal stability and low volatility to withstand processing

conditions. Preferably the compound will migrate to the surface of the fiber so as to minimize the amount of additive needed for adequate repellency. While this migration can often be enhanced by post-extrusion heating of the fiber, it is more preferable for the migration to occur without the need for this heating step. This requirement for mobility in the polymeric fiber in turn tends to limit the size of the fluorochemical molecule, and effectively eliminates from consideration high molecular weight polymeric fluorochemical additives.

The general concept of incorporating fluorochemical additives into a polyolefin fiber melt is known, but the difficulty in finding suitable effective additives has limited the application of this concept. Many of the past efforts to evaluate such fluorochemical additives have been aimed at improving other properties of the polyolefin, and do not teach methods of improving its repellency to low surface tension fluids.

Nonwoven composite structures are known consisting in part of two or more melt-extruded nonwoven layers, at least one of which includes an additive which imparts to the surface at least one characteristic different than the surface characteristics of the polymer alone as a result of preferential migration of the additive to the surface without the need for post-formation treatment of any kind. Examples of the additive-including layer include polypropylene modified

by commercially available fluorochemical additives, including "ZONYL" FTS defined above.

US Patent 5,178,931 and US Patent 5,178,932 disclose specific nonwoven laminiferous and composite structures respectively, consisting in part of three melt-extruded nonwoven layers, the second of which includes an additive which imparts alcohol repellency as a result of preferential migration of the additive to the surface without the need for post-formation treatment of any kind, and where at least one of the first and third layers has been treated by topical application of an agent to change its characteristics in some way. Examples of the additive included in the second layer include commercially available fluorochemicals, including "ZONYL" FTS.

Soil resistant polymeric compositions are known which are prepared by melt extrusion with a nonpolymeric fluorochemical dispersed throughout the polymer. The polymers used include polypropylene, polyethylene, polyamide and polyester, and the fluorochemical used is a perfluoroalkylstearate, in particular "ZONYL" FTS.

Japanese Patent Application 3-41160 to Kao Corp. teaches a thermoplastic resin composition containing a long chain fatty ester containing a perfluoroalkyl group of the formula R_f-R_1-OCO-R_2 wherein R_f is a perfluoroalkyl group with 5 to 16 carbons, R_1 is an alkylene group with 1 to 4 carbons, and R_2 is an unsaturated alkyl group or a saturated alkyl group with

21 to 50 carbons. The resins included polyethylene and polypropylene. Benefits of the additive were shown by the contact angle of water with molded articles of the resin. No tests were reported on the repellency of resulting polymers to low surface tension fluids.

In summary, while the prior art discloses numerous examples of polyolefin fibers containing a fluorochemical additive incorporated at the melt stage to alter the surface characteristics of the extruded fiber, much of this is directed at soiling and staining resistance or water repellency. Those references which disclose imparting alcohol repellency to polyolefin fabrics employ "ZONYL" FTS. A need exists to achieve superior repellency to low surface tension fluids and superior product efficiency. The fluorinated compounds of the present invention meet this need.

SUMMARY OF THE INVENTION

The present invention comprises a compound of formula A

$$R_f\text{-O-C(O)-}(CH_2)_n\text{-C(O)-O-}R_1 \qquad \text{A}$$

wherein

R_f is selected from the group consisting of

1) $F(CF_2)_x\text{-}(CH_2)_m$ wherein x is from about 4 to about 20, and m is from about 2 to about 6; and
2) $F(CF_2)_x\text{-}SO_2N(R_3)\text{-}R_4$ wherein x is a positive integer of from about 4 to about 20; R_3 is an alkyl radical of from

about 1 to about 4 carbon atoms; and R_4 is an alkylene radical of from about 1 to about 12 carbon atoms; and wherein R_1 is a saturated aliphatic hydrocarbon having from about 12 to about 66 carbon atoms; and n is 1 to about 20.

The present invention further comprises a compound of formula B

$$R_f\text{-}O\text{-}C(O)\text{-}CH_2\text{-}CH(R_2)\text{-}C(O)\text{-}O\text{-}R_f \qquad B$$

wherein each R_f is independently selected from the group consisting of

1) $F(CF_2)_x\text{-}(CH_2)_m$ wherein x is from about 4 to about 20, and m is from about 2 to about 6; and

2) $F(CF_2)_x\text{-}SO_2N(R_3)\text{-}R_4$ wherein x is a positive integer of from about 4 to about 20; R_3 is an alkyl radical of from about 1 to about 4 carbon atoms; and R_4 is an alkylene radical of from 1 to about 12 carbon atoms;

and wherein R_2 is a saturated or unsaturated hydrocarbon having from 1 to about 30 carbon atoms.

The present invention further comprises a mixture C comprising:

1) at least one compound of formula A

$$R_f\text{-}O\text{-}C(O)\text{-}(CH_2)_n\text{-}C(O)\text{-}O\text{-}R_1 \qquad A$$

2) at least one compound of formula D

$$R_f\text{-}O\text{-}C(O)\text{-}(CH_2)_n\text{-}C(O)\text{-}O\text{-}R_f \qquad D$$

3) at least one compound of formula E

$$R_1\text{-}O\text{-}C(O)\text{-}(CH_2)_n\text{-}C(O)\text{-}O\text{-}R_1 \qquad E$$

wherein each R_f is independently selected from the group consisting of

a) $F(CF_2)_x-(CH_2)_m$ wherein x is from about 4 to about 20, and m is from about 2 to about 6; and

b) $F(CF_2)_x-SO_2N(R_3)-R_4$ wherein x is a positive integer of from about 4 to about 20; R_3 is an alkyl radical of from 1 to about 4 carbon atoms; and R_4 is an alkylene radical of from 1 to about 12 carbon atoms;

and wherein each R_1 is independently a saturated aliphatic hydrocarbon having from about 12 to about 66 carbon atoms; and each n is independently 1 to about 20.

The present invention further comprises a compound of formula F

$$[F(CF_2)_xCH_2CH_2-S-CH_2]_2-C-[CH_2-O-C(O)-C_{17}H_{35}]_2 \quad F$$

wherein x is from about 4 to about 20.

The present invention further comprises a composition comprising 1) at least one of the compound of formula A, the compound of formula B, the mixture C, or the compound of formula F, each as defined above, and 2) at least one thermoplastic polymer.

The present invention further comprises a filament, fiber, film, molded article, or nonwoven web or fabric each comprising 1) at least one thermoplastic polymer and 2) at least one compound of formula A, compound of formula B, mixture C, or compound of formula F, each said compound or said mixture as defined above.

The present invention further comprises a process for imparting superior repellency of low surface tension fluids to thermoplastic polymer articles of manufacture comprising forming a mixture prior to article

formation of a polymer and an effective amount of an additive selected from the group consisting of a compound of formula A, a compound of formula B, a mixture C, or a compound of formula F, or mixtures thereof, as defined above, and melt extruding the mixture. This process is particularly suitable for imparting repellency of low surface tension fluids to polyolefin articles, and may be used either with or without post-extrusion heating of the article to promote movement of the additive to the article surface. The term "article" as used herein includes filaments, fibers, nonwoven webs or fabrics, films or molded articles.

DETAILED DESCRIPTION OF THE INVENTION

Superior repellency to low surface tension fluids is imparted to thermoplastic polymer articles, such as filaments, fibers, nonwovens, fabrics, films, or molded articles, by the addition of certain novel monomeric fluorinated diester compounds to a polymer prior to article formation and melt extruding the resulting mixture. This process is used either with or without post-extrusion heating of the article to promote movement of the additive to the article surface, since the diester compounds of this invention tend by their nature to concentrate on the surface.

The term "low surface tension fluids" is used herein to mean fluids having a surface tension of less than 50 dynes/cm (50×10^{-7} newton metre). Examples of

such fluids include alcohols, blood and certain body fluids.

The compounds of the present invention comprise the following groups of fluorinated diester compounds:

I. Fluorocarbon/hydrocarbon diesters of the formula A:

$$R_f\text{-O-C(O)-}(CH_2)_n\text{-C(O)-O-}R_1 \qquad A$$

II. Bis-fluorocarbon esters of the formula B:

$$R_f\text{-O-C(O)-}CH_2\text{-}CH(R_2)\text{-C(O)-O-}R_f \qquad B,$$

III. Mixture C comprising the diesters of formula A, the bis-esters of the fluorocarbon moieties of formula A represented by formula D, and the bis-esters of the hydrocarbon moieties of formula A represented by formula E.

$$R_f\text{-O-C(O)-}(CH_2)_n\text{-C(O)-O-}R_1 \qquad A$$

$$R_f\text{-O-C(O)-}(CH_2)_n\text{-C(O)-O-}R_f \qquad D$$

$$R_1\text{-O-C(O)-}(CH_2)_n\text{-C(O)-O-}R_1 \qquad E,$$

and

IV. Distearyl fluorocarbon esters of the formula F:

$$[F(CF_2)_xCH_2CH_2\text{-S-}CH_2]_2\text{-C-}[CH_2\text{-O-C(O)-}C_{17}H_{35}]_2 \qquad F$$

In the compounds and mixtures of this invention, R_f in the above formulae is $F(CF_2)_x\text{-}(CH_2)_m$ wherein x has a range of about 4 to about 20, and preferably an average value of from about 7 to about 10, and m has a value of 2 to 6. Especially preferred for R_f is a composition wherein the chain length distribution is as follows:

x=6 or less, 0-10% by weight

x=8, 45-75% by weight

$x=10$, 20-40% by weight

$x=12$, 1-20% by weight

$x=14$ or greater, 0-5% by weight.

This composition range, when $m=2$, is hereinafter referred to as Telomer BN. This definition of R_f in the formula R_f-OH is referred to as Telomer BN alcohol.

Alternatively in this invention, R_f is a fluorinated sulfonamide of the structure $F(CF_2)_x$-$SO_2N(R_3)$-R_4 wherein x is a positive integer from about 4 to about 20, preferably 4 to 10 inclusive; R_3 is an alkyl radical having from 1 to about 4 carbon atoms; and R_4 is an alkylene radical having from 1 to about 12 carbon atoms. Preferably R_3 is CH_3 and R_4 is $-CH_2CH_2-$, $-(CH_2)_3-$ or $-(CH_2)_4-$.

The fluoroalkyl portion of the alternative R_f structures is a fluorinated, preferably saturated, monovalent, non-aromatic, aliphatic radical of at least three fully fluorinated connected carbon atoms in a chain. The chain in the radical is straight, branched, or, if sufficiently large, cyclic and is optionally interrupted by divalent oxygen atoms, hexavalent sulfur atoms or trivalent nitrogen atoms bonded only to carbon atoms. A fully fluorinated aliphatic radical is preferred, but hydrogen or chlorine atoms are optionally present as substituents in the radical provided that not more than one atom of either is present in the radical for every two carbon atoms.

R_1 is a saturated aliphatic hydrocarbon with an average carbon chain length of from about 12 to about 66 carbons, preferably from about 24 to about 50 carbons. Alcohols corresponding to R_1-OH are commercially available from Petrolite Corporation, Polymers Division Headquarters, 6910 E. 14th Street, Tulsa, Oklahoma, U.S.A. 74112 under the trademark "UNILIN". "UNILIN" alcohols are fully saturated, long-chain linear alcohols. The approximate R_1 carbon atom ranges of "UNILIN" 350, 425, 550 and 700 are 12 to 50, 14 to 58, 16 to 56 and 14 to 66, respectively. The average chain lengths for "UNILIN" 350, 425, 550 and 700 are about 24, 32, 40 and 48, respectively. These are preferred for use in the present invention. More particularly the "UNILIN" carbon chain lengths are as noted in Table A:

TABLE A

		GC DATA**		
UNILIN	Lit. Avg.*	% Alcohol	Range	Average
350	C24-26		C12-46	C24-26
425	C30-32	85.0	C14-58	C30-32
550	C40-42	79.5	C16-56	C38
700	C48-50	83.6	C14-66	C50

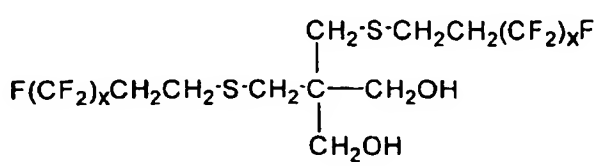
* Literature average

** Gas chromatography data

R_2 in formula B is a saturated or unsaturated hydrocarbon having from 1 to about 30 carbon atoms. Preferably R_2 is a straight or branched chain hydrocarbon of 12-18 carbon atoms and is saturated or mono-unsaturated. In the above formulas A, D and E, n has a value of 1 to about 20. In formula F, x is from about 4 to about 20.

There are various methods by which the above compounds can be prepared, and the inventive process is not limited to a particular method of preparation. For example, the compounds of formula A are conveniently made by reacting an appropriate fatty alcohol with the anhydride of an appropriate diacid to form an acid ester, which is first converted to the acid chloride and then reacted with an appropriate fluorinated alcohol. With this reaction sequence, the end product will have a fluorocarbon tail on one end of the molecule and a hydrocarbon tail on the other end, i.e substantially no diesters will have two fluorocarbon tails or two hydrocarbon tails. The compounds of formula B are conveniently made by reacting an appropriately substituted anhydride of a diacid with about 2 equivalents of an appropriate fluorinated alcohol. The compounds in mixture C are conveniently made by simultaneously reacting an appropriate diacid with one equivalent of the appropriate fluorinated alcohol and one equivalent of an appropriate fatty alcohol, or by sequentially reacting an anhydride of an appropriate diacid with the above two alcohols in either order.

The compounds of formula F are prepared by reacting stearic acid and a diol having the following structure:



Other compounds in these groups can readily be made by those skilled in the art by following similar processes.

The compounds and mixture of this invention are mixed with thermoplastic polymers by adding them to granular, pelletized, powdered or other appropriate forms of the polymers and rolling, agitating or compounding the mixture to achieve a uniform mixture which is then melt extruded. Alternatively the compounds of this invention are added to a polymer melt to form a mixture which is then melt extruded. The thermoplastic polymer is a polyolefin, polyester, polyamide, or polyacrylate. Preferably the thermoplatic polymer is a polyolefin, mixture or blend of one or more polyolefins, a polyolefin copolymer, mixture of polyolefin copolymers, or a mixture of at least one polyolefin and at least one polyolefin copolymer. The thermoplastic polymer is more preferably a polyolefin polymer or copolymer wherein the polymer unit or copolymer unit is ethylene, propylene or butylene or mixtures thereof. Thus the polyolefin is preferably polyethylene, polypropylene, polybutylene or a blend thereof or copolymers thereof.

The amount of the fluorinated compound added to the thermoplastic polymer is preferably between 0.1 and 5% by weight of the polymer. Amounts above this range can be used but are unnecessarily expensive in relation to the benefit received. Below this range the benefit is too small for practical use. The blend is then melted

and extruded into filaments, fibers, nonwoven fabrics or webs, films or molded articles using known methods. The fluorine content of the filament, fiber, nonwoven web or fabric prepared from said filament or fiber, film, or molded article is from about 200 µg/g to about 25,000 µg/g.

Extrusion is used to form various types of nonwovens. In particular, extrusion is used to form a melt blown nonwoven web of continuous and randomly deposited microfibers having an average diameter of approximately 0.1 to 10 microns, preferably in the range of about 3 to 5 microns. The melt extrusion is carried out through a die at a resin flow rate of at least 0.1 to 5 grams per minute per hole, with the microfibers being randomly deposited on a moving support to form the web.

In the above melt blowing process, polymer and a compound of the percent invention are fed into an extruder where it is melted and passed through a die containing a row of tiny orifices. As the polymer emerges from the die, it is contacted by two converging, high-velocity hot air streams, which attenuate the polymer into a blast of fine, discontinuous fibers of 0.1 to 10 microns in diameter. The useful polymer throughputs or flow rates range from 0.1 to 5 grams per minute per hole. Typical gas flow rates range from 2.5-100 psi (1.72×10^5 to 6.89×10^5 Pa) per minute of gas outlet area. The air temperature ranges from 400°F(204°C) to 750°F(399°C). Cooling air then quenches

the fibers, and they are deposited as a random, entangled web on a moving screen which is placed 6-12 inches (15.2-30.5 cm) in front of the blast of fibers.

Melt blowing processes are described in further detail in articles by V. A. Wente, "Superfine Thermoplastic Fibers", Industrial and Engineering Chemistry, Vol. 48(8), pp 1342-1346 (1956); and by R. R. Buntin and D. T. Lohkamp, "Melt Blowing - A One-step Web Process for New Nonwoven Products", Journal of the Technical Association of the Pulp and Paper Industry, Vol. 56(4), pp 74-77 (1973); as well as in US Patent 3,972,759 to R. R. Buntin. The disclosures of these documents are hereby incorporated by reference.

The unique properties of a melt blown nonwoven web comprised of a random array of fine, entangled fibers include very large surface areas, very small pore sizes, moderate strength and light weight fabric structure. These properties make the nonwoven webs particularly suitable for such applications as medical fabrics where barrier properties as well as breathability and drape are important.

Extrusion is used to form polymeric films. In film applications, a film-forming polymer and a compound of the present invention are simultaneously melted and mixed as they are conveyed through the extruder by a rotating screw or screws and then forced out through a slot or flat die, for example, where the film is quenched by a variety of techniques known to those skilled in the

art. The films optionally are oriented prior to quenching by drawing or stretching the film at elevated temperatures.

Molded articles are produced by pressing or injecting molten polymer containing a compound of the present invention from a melt extruder as described above into a mold where the polymer solidifies. Typical melt forming techniques include injection molding, blow molding, compression molding and extrusion, and are well known to those skilled in the art. The molded article is then ejected from the mold and optionally, heat-treated to effect migration of the polymer additives to the surface of the article.

An optional heating or annealing step can be conducted but is not required. The polymer melt or extruded fiber, filament, nonwoven web or fabric, film, or molded article is heated to a temperature of from about 25°C to about 150°C. The heating in some cases may improve the effectiveness of the fluorochemical additive in imparting alcohol repellency.

The compounds, mixtures, and compositions of the present invention are useful in various filaments, fibers, nonwoven webs or fabrics, films and molded articles. Examples include fibers for use in fabrics and carpets, nonwoven fabrics used in protective garments used in the medical/surgical field, and molded plastic articles of many types. The process of the present invention is useful for imparting repellency of low

surface tension fluids to various thermoplastic polymer articles such as filaments, fibers, nonwoven webs or fabrics, films and molded articles.

EXAMPLES

Example 1

Synthesis of R_f-O-C(O)-$(CH_2)_n$-C(O)-O-R_1, wherein R_f is an aliphatic fluorocarbon radical of formula $F(CF_2)_x(CH_2)_m$ where the average value of x is 9, m=2, n=2, and wherein R_1 has an average value of 24 carbon atoms.

Step A

A 2-liter 4-necked flask was equipped with mechanical agitation, a temperature control device, Dean-Stark trap, water condenser, and nitrogen gas inlet and outlet tubes. It was charged with 600mL of toluene which was then heated at reflux for one hour to remove traces of water. After the toluene was cooled, 103.2g (1.0 mole) succinic anhydride and 435.0g (1.0 mole) "UNILIN" 350 alcohol were added. The mixture was heated at reflux for 4 hours and cooled. The toluene was removed by rotary evaporation. The product was dried in a vacuum oven at 50°C for 18 hours yielding 532.8g (99% yield) of white waxy solid.

Step B

A dry 5-liter 4-necked flask was equipped with mechanical agitation, temperature control device and a water condenser fitted with a drying tube connected to both a nitrogen gas inlet tube and caustic scrubber with

a nitrogen gas outlet. It was charged with 403.4g (0.754 mole) $H(CH_2)_{24}$-O-C(O)-$(CH_2)_2$-COOH from Step A, 3L of 1,2-dichloroethane, 2.5g (0.011 mole) benzyltriethylammonium chloride and 55mL (0.754 mole) thionyl chloride. The reaction mixture was heated at reflux for 3 hours, and after being cooled to 70°C, 397.4g (0.754 mole) of Telomer BN alcohol was added. The reaction mixture was then cooled to 35°C and 87.7g (0.867 mole) of triethylamine was added dropwise over 2 hours. After the addition was complete, the mixture was held at 35°C for 3 hours and then heated at 60°C for 1 hour. At room temperature, the reaction mixture was filtered and the solid product air-dried, slurried in 5L isopropyl alcohol at 60°C for 1 hour, filtered, and washed with deionized water and with isopropyl alcohol. The product was recrystallized in portions from isopropyl alcohol yielding 447.1g (57% yield) off-white solid; m.p. 83.8°C by DSC (Differential Scanning Calorimetry). The percent fluorine found was 32.5%; the percent fluorine calculated was 33.9%.

Example 2

Synthesis of R_f-O-C(O)-CH_2-CH(CH_2CH=$CHC_{15}H_{31}$)-C(O)-O-R_f where R_f is an aliphatic fluorocarbon radical of formula $F(CF_2)_x(CH_2)_m$ where the average value of x is 9, and m=2.

A 250-mL flask was equipped with mechanical agitation, a temperature control device, water condenser, Dean-Stark trap and nitrogen gas inlet and outlet tubes. It was charged with 28.3g (0.08 mole) octadecenylsuccinic

anhydride (acid # 317.4mg KOH/g cmpd), 84.2g (0.16 mole) Telomer BN alcohol, 0.2g phosphorous acid (70%) and 0.08g boric acid. The mixture was heated at 140-145°C for approximately 48 hours. A tan, waxy solid was isolated weighing 102.1g (91.9% yield); m.p. 42.4°C (by DSC); percent fluorine found was 49.2%; percent fluorine calculated was 50.9%.

Example 3

Synthesis of mixture of R_f-O-C(O)-$(CH_2)_n$-C(O)-O-R_1, R_f-O-C(O)-$(CH_2)_n$-C(O)-O-R_f, and R_1-O-C(O)-$(CH_2)_n$-C(O)-O-R_1, where R_f is an aliphatic fluorocarbon radical of formula $F(CF_2)_x(CH_2)_m$ where the average value of x is 9, m=2, n=10, and R_1 has an average value of 24 carbon atoms.

The apparatus of Example 2 was charged with 43.5g (0.1 mole) UNILIN 350 alcohol, 61.0g (0.11 mole) Telomer BN alcohol, 23.0g (0.1 mole) 1,12-dodecanedioic acid, 0.5g 70% phosphorous acid and 0.2g boric acid. The mixture was heated at 140°C for approximately 150 hours. A tan waxy solid was isolated, m.p. 61.8°C (by DSC); percent fluorine found 31.8, percent fluorine calculated 34.0%.

Example 4

Synthesis of a mixture similar to that in Example 3 except that an alternative preparative method was used, and that n=2.

Step A

A 1-liter 4-necked flask was equipped with mechanical agitation, a temperature control device, water condenser, Dean-Stark trap and nitrogen gas inlet and outlet tubes. It was charged with 300mL toluene, 41.3g (0.4 mole) succinic anhydride (97%) and 210.8g (0.4 mole) Telomer BN alcohol. The mixture was heated at reflux for 4 hours and then cooled to 60°C. The toluene was removed by rotary evaporation, and the off-white solid product was dried in a vacuum oven at 50°C for approximately 18 hours yielding 225.1 grams (89.3% yield).

Step B

A 100mL 4-necked flask was equipped with mechanical agitation, a temperature control device, water condenser, Dean-Stark trap and nitrogen gas inlet and outlet tubes. It was charged with 60.5g (0.1 mole) $F(CF_2)_x(CH_2)_2$-OC(O)-$(CH_2)_2$-COOH from Step A above, 43.5g (0.1 mole) "UNILIN" 350 alcohol, 0.2g 70% phosphorous acid and 0.08g boric acid. The reaction mixture was heated at 140°C for approximately 48 hours. A tan waxy solid was recovered, m.p. 50.5°C (by DSC); percent fluorine found was 33.2%, percent fluorine calculated was 35.3%.

Example 5

Step 1: Preparation of the polymer blend

Uniform mixtures of the fluorochemical additives produced in Examples 1 through 4 together with a polyolefin were prepared by combining them and rolling

the mixture for 24 hours. The polyolefin used was Escorene PD3545G or PD3746G (Exxon Chemical Americas, P.O. Box 3273, Houston, Texas 77001) polypropylene resin having a melt flow rate of approximately 800 and 1,000 respectively). The composition and calculated fluorine concentrations of the mixtures are given in the Table 1. Two comparative examples using compounds described in prior art were prepared in a similar manner. Comparative Example 1 used the mono-ester "ZONYL" FTS; Comparative Example 2 used the bis-fluorocarbon ester made from Telomer BN alcohol and dodecanedioic acid.

Table 1

Example #	Additive (g)	Polyolefin (g)	ppm F calc'd
1	14.1	1348	0.330
2	11.1	1351	0.400
3	16.0	1346	0.373
4	17.6	1344	0.429
Comp.Ex.1	16.2	1800	0.400
Comp.Ex.2	2.2	452	0.300

Step 2: Melt blown web formation

Melt blown nonwoven webs were prepared from the above mixtures using a 6-inch (15 cm) melt blowing pilot unit at a polymer feed rate of about 0.4 gram/minute/hole. The polymer blends were fed into the extruder having three barrel zones at temperatures ranging from 175°C to 250°C. The temperature at the die was 232 to 254°C and the air temperature was 260 to 271°C. The die tip gap was 0.060 inches (0.15 cm) and the primary air pressure was 2.6 psi (17.9 x 10^3 Pa).

The webs were formed on a drum coated with "TEFLON" and collected on a take-up roll operating at 30 feet/minute (914 cm/minute) which resulted in the fabrics having a basis weight of 1.0 oz./square yard (34 gram/square meter).

Step 3. Repellency testing

The water repellent properties of the melt blown webs were measured using an isopropyl alcohol/water test and are expressed in terms of percent isopropyl alcohol repellency. Webs that resist penetration of a 100% isopropyl alcohol/0% water solution (lowest surface tension fluid) after 1-2 minutes are given the highest rating of 100. Webs that are only resistant to a 100% water/0% isopropyl alcohol solution after 1-2 minutes are given the lowest rating of 0. Intermediate ratings of 20 to 90 in increments of 10 correspond to solutions of 20% isopropyl alcohol/80% water to solutions of 90% isopropyl alcohol/10% water. The isopropyl alcohol repellency rating for a given fabric corresponds to the lowest surface tension fluid (greatest % isopropyl alcohol/water solution) that does not wet the fabric after 1-2 minutes.

To evaluate in-process repellency, the webs were rated immediately after exiting the melt blown line and then at time intervals of 1 hour, 1 day, 12 days and after heating at 140°F (60°C) for 22 hours. Table 2 summarizes the isopropyl alcohol repellency data for the polypropylene melt blown webs containing Examples 1, 2, 3

and 4 and the two comparison examples. Also included in the table is a polypropylene control sample.

Table 2

% Isopropyl Alcohol Repellency of Polypropylene Melt Blown Webs

		% Repellency				
Example	μg/g Fluorine	In-Process	After 1 Hr	After 1 day	After 12 days	Heated 60°C/22hr
1	3290	60-70	80	90	100	100
2	3030	60-70	70	-	70	70
3	3140	30-50	60	80	90	90
4	2910	50	60	-	90	80
Comp. 1	2590	30	30	30	60	40
Comp. 2	1750	20	20	20	20	-
Control		20	20	20	20	

The above results showed the clear advantage of the inventive compositions over the comparative and control samples, the advantages showing up immediately and over time. A related advantage for the inventive compositions was their lower fluorine loss during melt extrusion processing, as shown by comparing the fluorine analyses in the above Table 2 with those in Table 1. The additives in Comparative Examples 1 and 2 showed losses of 35% and 42%, respectively, while the additives in Examples 1, 2, 3 and 4 showed lower fluorine losses of 1%, 24%, 16% and 32%, respectively, contributing to their better performance.

Example 6

A 500-ml round bottom flask equipped with a mechanical agitator, temperature control device, Dean-Stark trap, water condenser, and nitrogen inlet/outlet tubes was charged with 132.5 g (0.11 mole) of a bis(perfluoroalkylethylmercapto)neopentylglycol mixture of the formula $[F(CF_2)_xCH_2CH_2SCH_2]_2C(CH_2OH)_2$, wherein x

is predominantly 8, 10 and 12, 78.2 g (0.275 mole) stearic acid, 10 g "AMBERLYST" 15 ion-exchange resin and 80 g 'Baker analyzed' xylenes. The Dean-Stark trap was filled to overflow with xylenes and the reaction flask contents then stirred at reflux. Additional fluoroglycol (10.3 g and 22.3 g, respectively), was added to the reaction mass after 16 hours and 32 hours at reflux. After a total of 48 hours reflux, the reaction mass was filtered to remove the ion-exchange resin and desolvated by rotary evaporation to recover a 40.5% fluorine content flaky solid.

A polymer blend and melt blown nonwoven web were prepared as in Example 5. Repellency testing was conducted on the web using the procedure detailed in Example 5. The resulting data are summarized in Table 3. These results showed the clear advantage of the inventive compositions of formula F over the comparative examples listed in Table 2.

Table 3

%Isopropyl Alcohol Repellency of Melt Blown Webs

μg/g	% Repellency				
fluorine	In-process	After 1 hr	After 1 day	After 12 days	Heated
3330	80	90	90	90	90[1]
1970	70	70	-	90*	80[2]
1440	50	50	-	80*	70[2]

* after 3 days

1 140°F (60°C)/22 hr.
2 176°F (80°C) 15 sec.

What is claimed is:

1. A compound of formula A

$$R_f\text{-O-C(O)-(CH}_2)_n\text{-C(O)-O-}R_1 \qquad A$$

wherein

Rf is selected from the group consisting of

1) $F(CF_2)_x\text{-}(CH_2)_m$ wherein x is from about 4 to about 20, and m is from about 2 to about 6; and

2) $F(CF_2)_x\text{-}SO_2N(R_3)\text{-}R_4$ wherein x is a positive integer of from about 4 to about 20; R_3 is an alkyl radical of from about 1 to about 4 carbon atoms; and R_4 is an alkylene radical of from about 1 to about 12 carbon atoms;

R_1 is a saturated aliphatic hydrocarbon having from about 12 to about 66 carbon atoms; and

n is 1 to about 20.

2. A compound of formula B

$$R_f\text{-O-C(O)-CH}_2\text{-CH(}R_2\text{)-C(O)-O-}R_f \qquad B$$

wherein

each R_f is independently selected from the group consisting of

1) $F(CF_2)_x\text{-}(CH_2)_m$ wherein x is from about 4 to about 20, and m is from about 2 to about 6; and

2) $F(CF_2)_x\text{-}SO_2N(R_3)\text{-}R_4$ wherein x is a positive integer of from about 4 to about 20; R_3 is an alkyl radical of from about 1 to about 4 carbon atoms; and R_4 is an alkylene radical of from 1 to about 20 carbon atoms; and

R_2 is a saturated or unsaturated hydrocarbon having from 1 to about 30 carbon atoms.

3. A mixture C comprising

1) at least one compound of formula A

$$R_f\text{-O-C(O)-}(CH_2)_n\text{-C(O)-O-}R_1 \qquad A$$

2) at least one compound of formula D

$$R_f\text{-O-C(O)-}(CH_2)_n\text{-C(O)-O-}R_f \qquad D \quad \text{and}$$

3) at least one compound of formula E

$$R_1\text{-O-C(O)-}(CH_2)_n\text{-C(O)-O-}R_1 \qquad E$$

wherein

each R_f is independently selected from the group consisting of

a) $F(CF_2)_x\text{-}(CH_2)_m$ wherein x is from about 4 to about 20, and m is from about 2 to about 6; and

b) $F(CF_2)x\text{-}SO_2N(R_3)\text{-}R_4$ wherein x is a positive integer of from about 4 to about 20; R_3 is an alkyl radical of from 1 to about 4 carbon atoms; and R_4 is an alkylene radical of from 1 to about 12 carbon atoms;

each R_1 is independently a saturated aliphatic hydrocarbon having from about 12 to about 66 carbon atoms; and

each n is independently 1 to about 20.

4. A compound of formula F

$$[F(CF_2)_xCH_2CH_2\text{-S-}CH_2]_2\text{-C-}[CH_2\text{-O-C(O)-}C_{17}H_{35}]_2 \quad F$$

wherein x is from about 4 to about 20.

5. A composition comprising at least one thermoplastic polymer selected from the group consisting of polyolefin, polyester, polyamide and polyacrylate, and at least one compound or mixture selected from the group consisting of

I) a compound of formula A

$$R_f\text{-O-C(O)-}(CH_2)_n\text{-C(O)-O-}R_1 \qquad A$$

wherein

Rf is selected from the group consisting of

1) $F(CF_2)_x\text{-}(CH_2)_m$ wherein x is from about 4 to about 20, and m is from about 2 to about 6; and

2) $F(CF_2)_x\text{-}SO_2N(R_3)\text{-}R_4$ wherein x is a positive integer of from about 4 to about 20; R_3 is an alkyl radical of from about 1 to about 4 carbon atoms; and R_4 is an alkylene radical of from about 1 to about 12 carbon atoms;

R_1 is a saturated aliphatic hydrocarbon having from about 12 to about 66 carbon atoms; and

n is 1 to about 20;

II) a compound of formula B

$$R_f\text{-O-C(O)-}CH_2\text{-}CH(R_2)\text{-C(O)-O-}R_f \qquad B$$

wherein

each R_f is as defined above for formula A, and

R_2 is a saturated or unsaturated hydrocarbon having from 1 to about 30 carbon atoms;

III) a mixture C comprising

1) at least one compound of formula A

$$R_f\text{-O-C(O)-}(CH_2)_n\text{-C(O)-O-}R_1 \qquad A$$

2) at least one compound of formula D

$$R_f\text{-O-C(O)-(CH}_2)_n\text{-C(O)-O-}R_f \qquad D \qquad \text{and}$$

3) at least one compound of formula E

$$R_1\text{-O-C(O)-(CH}_2)_n\text{-C(O)-O-}R_1 \qquad E$$

wherein

each R_f, R_1, and n are as defined above for formula A; and

IV) a compound of formula F

$$[F(CF_2)_xCH_2CH_2\text{-S-}CH_2]_2\text{-C-}[CH_2\text{-O-C(O)-}C_{17}H_{35}]_2 \qquad F$$

wherein x is from about 4 to about 20.

6. The composition of Claim 5 wherein the thermoplastic polymer has dispersed therein from about 0.1% to about 5% by weight of polymer of said compound or mixture, and wherein said compound or mixture improves repellency to low surface tension fluids.

7. The composition of Claim 6 in the form of an extruded filament, nonwoven fabric, film, or molded article, said composition having a fluorine content of from about 200 μg/g to about 25,000 μg/g.

8. A process for imparting repellency of low surface tension fluids to a thermoplastic polymer article comprising forming a mixture prior to article formation

of a polymer and an effective amount of an additive selected from the group consisting of

I) a compound of formula A

$$R_f\text{-O-C(O)-(CH}_2)_n\text{-C(O)-O-}R_1 \qquad \text{A}$$

wherein

Rf is selected from the group consisting of

1) $F(CF_2)_x\text{-}(CH_2)_m$ wherein x is from about 4 to about 20, and m is from about 2 to about 6; and

2) $F(CF_2)_x\text{-}SO_2N(R_3)\text{-}R_4$ wherein x is a positive integer of from about 4 to about 20; R_3 is an alkyl radical of from about 1 to about 4 carbon atoms; and R_4 is an alkylene radical of from about 1 to about 12 carbon atoms;

R_1 is a saturated aliphatic hydrocarbon having from about 12 to about 66 carbon atoms; and

n is 1 to about 20;

II) a compound of formula B

$$R_f\text{-O-C(O)-CH}_2\text{-CH(}R_2\text{)-C(O)-O-}R_f \qquad \text{B}$$

wherein

each R_f is as defined above for formula A, and

R_2 is a saturated or unsaturated hydrocarbon having from 1 to about 30 carbon atoms;

III) a mixture C comprising

1) at least one compound of formula A

$$R_f\text{-O-C(O)-(CH}_2)_n\text{-C(O)-O-}R_1 \qquad \text{A}$$

2) at least one compound of formula D

$$R_f\text{-O-C(O)-(CH}_2)_n\text{-C(O)-O-}R_f \qquad \text{D} \quad \text{and}$$

3) at least one compound of formula E

$$R_1\text{-O-C(O)-(CH}_2)_n\text{-C(O)-O-}R_1 \qquad E$$

wherein

each R_f, R_1, and n are as defined above for formula A; and

IV) a compound of formula F

$$[F(CF_2)_xCH_2CH_2\text{-S-}CH_2]_2\text{-C-}[CH_2\text{-O-C(O)-}C_{17}H_{35}]_2 \qquad F$$

wherein x is from about 4 to about 20; and melt extruding the mixture.

9. The process of Claim 8 further comprising heating the formed article to a temperature of from about 25°C to about 150°C after addition of the additive.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 96/20541

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C07C69/63 C07C323/03 C08K5/11 D01F1/10 D06M13/265
C07C311/09 C07C323/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C07C C08K D01F D06M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 07 330 673 A (KAO CORP) 19 December 1995 see compounds 2a, 2b, 2c, 2d ---	1
X	US 3 716 401 A (AXELROD R) 13 February 1973 see column 8, line 45 - line 52	1
X	see column 7, line 25 - line 30 ---	5
X	JP 63 045 238 A (SONY CORP) 26 February 1988 see claim 2; example 9 ---	1
P,X	JP 08 269 342 A (ASAHI GLASS KK) 15 October 1996 see paragraph 114 - paragraph 118 --- -/--	1

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

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"&" document member of the same patent family

1

Date of the actual completion of the international search	Date of mailing of the international search report
25 March 1997	21.04.97

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Schueler, D

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Intern   al Application No
PCT/US 96/20541

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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P,X	JP 08 259 501 A (HITACHI MAXELL KK) 8 October 1996 see page 2; figure 1 ---	1
A	DE 22 39 709 A (PENNWALT CORP) 22 February 1973 see claims -----	4

1

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